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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 14 September 1994	3. REPORT TYPE AND DATES COVERED Annual Technical Report: 93/10/01-94/09/30
4. TITLE AND SUBTITLE Chemistry Involving the Preparation, Isolation, and Immobilization of III-V Compound Semiconductor Nanocrystals and Quantum Dots		5. FUNDING NUMBERS F49620-93-1-0004 6110&F 2303/B S
6. AUTHOR(S) Richard L. Wells and Louis A. Coury		7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(E) Department of Chemistry Duke University Durham, NC 27708-0346
8. PERFORMING ORGANIZATION REPORT NUMBER Annual Technical Report No. DU/DC/ATR-02 AFOSR-TR- 94 0685		9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) NL AFOSR/AC and AFOSR/PKA 110 Duncan Avenue, Suite B115 Boling Air Force Base, DC 20332-0001
10. SPONSORING / MONITORING AGENCY REPORT NUMBER 19941129 078		11. SUPPLEMENTARY NOTES
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution Unlimited		12b. DISTRIBUTION CODE A
13. ABSTRACT (Maximum 200 words)  The facile thermolysis of $[Cl_2GaP(SiMe_3)_2]_2$ to eliminate $Me_3SiX$ and yield nanocrystalline GaP has been studied via thermal gravimetric analysis (TGA) and it has been found that the $Me_3SiCl$ is eliminated in a step-wise manner. Also, the new ternary single-source precursor $[Ga_2(As,P)Cl_3]_n$ has been synthesized and thermolyzed to yield the ternary III-V $GaAs_xPy$ . In addition, nanocrystalline GaAs and GaP, prepared by the Kher/Wells low temperature solution phase method, have been studied by transmission electron microscopy (TEM) and, in the TEM's of both, the lattice fringes of nanocrystalline material are clearly evident. Using a host of analytical techniques, it has been shown that the GaAs has crystalline regions of $12 \pm 2$ nm. In addition, efforts in immobilization of particles have involved all binary permutations of In and Ga phosphides and arsenides. The materials have been cast onto electrode surfaces from volatile solvents to give uniform deposits. Dispersions can also be created in the presence of monomers which are subsequently electropolymerized to prepare composite films. In an STM plot of InAs immobilized in a poly(pyrrole) film, the nanocrystals appear as yellow dots embedded in the brown film, indicating that they extend above the film, and/or have a higher conductivity than the polymer.		
DTIC QUALITY INSPECTED 5		
14. SUBJECT TERMS Synthesis, Ternary Single-Source Precursor, III-V Nanocrystals, III-V Quantum Dots, Characterization, Immobilization		15. NUMBER OF PAGES 11
		16. PRICE CODE 12
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified
		20. LIMITATION OF ABSTRACT Unlimited

Principal Investigator Annual Data Collection (PIADC) Survey Form

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PI DATA

Name (Last, First, MI): Wells, Richard L.  
Institution: Duke University  
Contract/Grant No.: F49620-93-1-0004  
Co-Pi: Courv. Louis A.  
Institution: Duke University

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Project/Subarea: 2503/BS  
NX NC  
FY 94

CONTRACT/GRANT CO-INVESTIGATORS (Quantities - by Type- Include Self)

Post Doctorates 1 Graduates 2 Other 2 (PI & Co-PI)

ARTICLES/BOOKS PUBLISHED RELATED TO AFOREMENTIONED CONTRACT/GRANT

NOTE 1: List all individual's names in the following format (Last Name, First Name, Middle Initial).

NOTE 2: Only include publications in peer reviewed professional journals and refereed book chapters.  
Do not include: Abstracts, "Scientific American" type articles, or articles that are not primary reports of new data, and articles submitted or accepted for publication, but with a publication date outside the stated time frame.

JOURNAL or BOOK (Circle one) Publisher: American Chemical Society

Journal/Book Name: Chemistry of Materials

Journal/Book Author: Aubuchon, S.R.; McPhail, A.T.; Wells, R.L.; Giambra, J.A.; and Bowser, J.R.

Subject Author: "Preparation, Characterization and Facile Thermolysis of  $[X_2GaP(SiMe_3)_2]_2$ , (X = Br, I) and  $(Cl_3Ga_2P)_n$ : New Precursors to Nanocrystalline Gallium Phosphide"

Journal Volume/Book Chapter: 6 Month Published: January Year Published: 1994

pp. 82 - 86

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ARTICLES/BOOKS PUBLISHED RELATED TO AFOREMENTIONED CONTRACT/GRANT (Cont.)

**JOURNAL or BOOK**  
(Circle one)

Publisher: Pergamon Press

Journal/Book Name: Polyhedron

Journal/Book Author: Sir G. Wilkinson, Editor

Subject Title: "Synthesis and Molecular Structures of R(Me<sub>2</sub>CCH<sub>2</sub>)<sub>2</sub>In-E(SiMe<sub>3</sub>)<sub>3</sub> (R = Me, CCH<sub>3</sub>, E = P or As; R = Me, E = P)"

Subject Author: Self, M.F.; McPhail, A.T.; Jones III, L.J.; and Wells, R.L.

Journal Volume/Book Chapter: 13 Month Published: February Year Published: 1994  
pp. 625-634.

**JOURNAL or BOOK**  
(Circle one)

Publisher: Materials Research Society

Journal/Book Name: Materials Research Society Symposium Proceedings

Journal/Book Author: Cammerata, R.C.; and Gonsalves, K.E.; Eds.

Subject Title: "A Low Temperature, Solution Phase Synthesis of III-V Semiconductor Nanocrystals"

Subject Author: Kher, S.S.; and Wells, R.L.

Journal Volume/Book Chapter: 351 Month Published: September Year Published: 1994  
pp. 293-298.

**JOURNAL or BOOK**  
(Circle one)

Publisher: \_\_\_\_\_

Journal/Book Name: \_\_\_\_\_

Journal/Book Author: \_\_\_\_\_

Subject Title: \_\_\_\_\_

Subject Author: \_\_\_\_\_

Journal Volume/Book Chapter: \_\_\_\_\_ Month Published: \_\_\_\_\_ Year Published: \_\_\_\_\_

HONORS/AWARDS RECEIVED RELATED TO AFOREMENTIONED CONTRACT/GRANT

Honor/Award: Joe Taylor Adams Fellowship Year Received: 1994

Honor/Award Recipient(s): Steven R. Aubuchon

Awarding Organization: Department of Chemistry, Duke University

Honor/Award: \_\_\_\_\_ Year Received: \_\_\_\_\_

Honor/Award Recipient(s): \_\_\_\_\_

Awarding Organization: \_\_\_\_\_

Honor/Award: \_\_\_\_\_ Year Received: \_\_\_\_\_

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Awarding Organization: \_\_\_\_\_

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Awarding Organization: \_\_\_\_\_

**Research Highlights - For the Period 1 October 1993 through 30 September 1994**

**R. L. Wells and L. A. Coury,**

**Department of Chemistry, Duke University, Durham, NC**

**Explanatory Notes**

**Vugraph 1 - Introduction**

Recent research in Professor Wells' laboratories at Duke University has demonstrated the utility of silyl cleavage by showing that reactions between  $\text{GaCl}_3$  and  $\text{As}(\text{SiMe}_3)_3$  or  $\text{P}(\text{SiMe}_3)_3$  in hydrocarbon solvents yield nanocrystalline  $\text{GaAs}$  or new cyclic precursors which can be thermally decomposed to yield nanocrystalline  $\text{GaP}$  (vu 1, eq 1). Two other research groups have utilized the silyl cleavage reaction to synthesize  $\text{GaAs}$  nanocrystals in quinoline. In addition, Uchida *et al.* reported the synthesis of  $\text{GaAs}$  and  $\text{InAs}$  nanocrystals from  $\text{Ga}(\text{acac})_3$  and  $\text{In}(\text{acac})_3$ , respectively, by reactions with  $\text{As}(\text{SiMe}_3)_3$ , however, formation of by-products or the fate of the acetylacetone ligands were not reported (vu 1, eq 2). In addition, it has been demonstrated by the Wells group that  $\text{GaCl}_3$  and  $\text{As}(\text{SiMe}_3)_3$  or  $\text{P}(\text{SiMe}_3)_3$  mixed in a 2:1 ratio react to yield in each case a stable substance having the empirical formula  $\text{Ga}_2\text{ECl}_3$  ( $\text{E} = \text{As}$  or  $\text{P}$ ) (vu 1, eq 3). These substances eliminate  $\text{GaCl}_3$  at elevated temperatures to give nanocrystalline  $\text{GaAs}$  and  $\text{GaP}$ , respectively (vu 1, eq 3).

Recently Kaner and co-workers reported a general method involving solid state metathesis (SSM) to synthesize binary III-V semiconductors by reacting sodium pnictides with Group III trihalides either in bombs or sealed glass ampules at high temperatures (vu 1, eqs 4 and 5). These exothermic reactions generate enough heat to melt the sodium halide product and, therefore, SSM reactions yield polycrystalline III-V semiconductors often contaminated with starting materials and by-products. It has also been reported that the III-V materials produced by this method contain considerable amounts of non-removable halide inclusions and the rapid exothermic SSM reactions introduce high defect concentration and lattice strain in resulting materials.

**Vugraph 2 - Research Highlight One**

The previously mentioned (see above, sentence 1) new cyclic compounds with Ga-P containing cores and exocyclic halogen ligands on the metal centers undergo facile thermolysis to eliminate  $\text{Me}_3\text{SiX}$  and yield nanocrystalline  $\text{GaP}$  (vu 2, eq). This thermolysis can be studied *via* thermal gravimetric analysis (TGA). The TGA of the chlorine-containing cyclic compound, which is shown on viewgraph 2, clearly exhibits separate transitions, corresponding to a stepwise elimination of  $\text{Me}_3\text{SiCl}$ .

**Viewgraph 3 - Research Highlight Two**

As noted on the introductory viewgraph, Wells and co-workers has reported the synthesis of single-source precursors of the general formula  $(\text{Ga}_2\text{ECl}_3)_n$  which can be thermolyzed to yield nanocrystalline binary semiconductor materials. As illustrated by equations 1 and 2 on vugraph 3, they have now applied this methodology to the synthesis of a single-source precursor to a ternary III-V, namely, gallium arsenide phosphide. The figure shown on viewgraph 3 compares the diffraction patterns of

GaAs, GaP and  $\text{GaA}_x\text{P}_y$ , all prepared using the same methodology/technique. The ternary material exhibits hybrid characteristics of the two binaries, with d-spacing values directly between those of GaAs and GaP. This is conclusive evidence for a semiconductor solid-solution, according to Vegard's Law.

#### Viewgraph 4 - Research Highlight Three

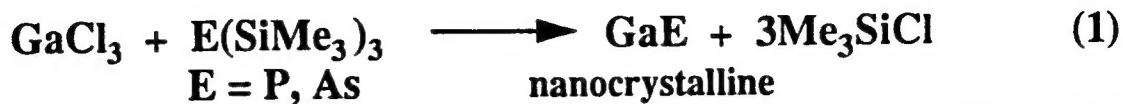
Kher and Wells have reported the development of a new, low temperature solution phase synthesis of nanocrystalline III-V semiconductors. Their methodology involves *in situ* formation of the sodium/potassium pnictide, followed by reaction with the metal halide to form the semiconductor quantum dots (see vu 4, eqs 1 and 2). These materials have been studied by transmission electron microscopy (TEM). In the TEM's shown on viewgraph 4, the lattice fringes of nanocrystalline GaAs and GaP are clearly evident.

#### Viewgraph 5 - Research Highlight Four

Co-PI Coury and coworkers have conducted the first characterization of nanocrystalline GaAs prepared by the solution metathesis reaction of Kher and Wells. Using a host of analytical techniques, they have shown that this material has crystalline regions of  $12 \pm 2$  nm. The particles themselves are of similar total size, and are roughly spherical in shape. The as-prepared material is relatively free of surface oxides, although prolonged exposure to water results in the formation of soluble, acidic arsenic compounds, detectable by electrochemical techniques. High resolution electron microscopy showed that aggregates of the particles can be dispersed by sonication, but that the nanocrystalline lattices remain unaffected by ultrasound. The particles appear to be relatively conductive, since they obtained stable images by scanning tunneling microscopy (STM) using similar bias voltages to those employed for imaging bulk GaAs wafers. Finally, very recent solid-state luminescence measurements have revealed clear evidence for quantum confinement through blue-shifted emission maxima. Our efforts in immobilization of the particles have involved all binary permutations of In and Ga phosphides and arsenides. These materials can be cast onto electrode surfaces from volatile solvents to give uniform deposits. Dispersions can also be created in the presence of monomers which are subsequently electropolymerized to prepare composite films. Image A on viewgraph 5 shows the STM of a conductive poly(pyrrole) film grown on a Pt electrode. The image is relatively featureless, indicating a smooth, uniform film. By comparison, InAs crystals deposited from a methanol suspension are shown in image B on a scale of  $400 \times 400$  nm. The particles are easily visible and are of uniform size, as seen in the profilometer trace (top). Image C shows the STM of InAs immobilized in a poly(pyrrole) film. In this plot, the nanocrystals appear as yellow dots embedded in the brown film, indicating that they extend above the film, and/or have a higher conductivity than the polymer.

## Introduction

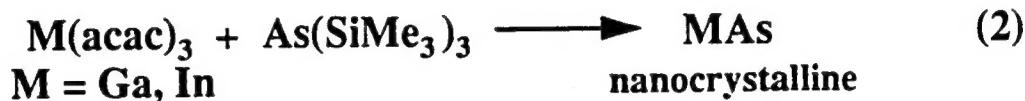
## Syntheses of III-V Nanocrystals



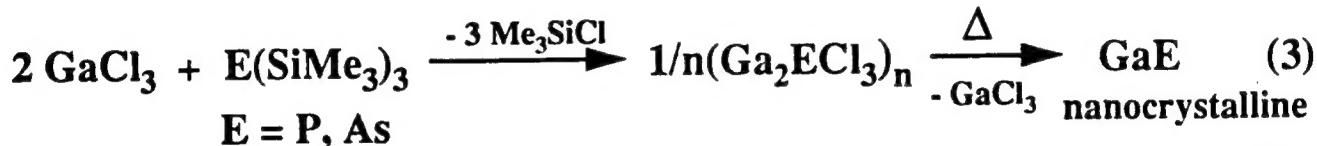
Wells and co-workers (a) *Chem. Mater.* 1989, 1, 4; (b) *Mater. Res. Soc. Symp. Proc.* 1989, 131, 45; (c) *Chem. Mater.* 1991, 3, 382; (d) *Organometallics* 1993, 12, 2832; (e) *Chem. Mater.* 1994, 6, 82.

Alivisatos and co-workers *J. Am. Chem. Soc.* 1990, **112**, 9438.

Uchida et al. *J. Phys. Chem.* 1991, 95, 5382.



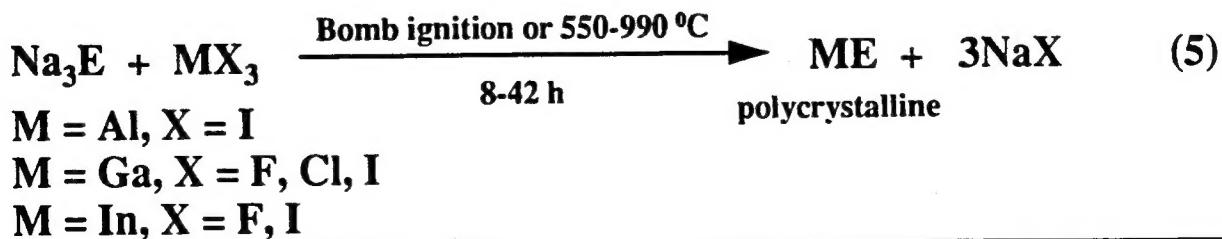
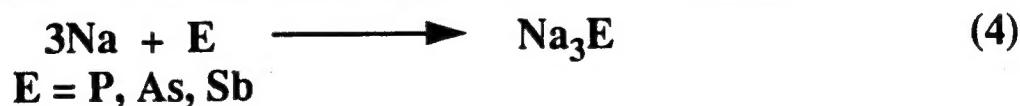
Uchida et al. (a) *J. Phys. Chem.* 1992, 96, 1156; (b) *Chem. Mater.* 1993, 5, 716



Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Woudenberg, R. C.; Jasinski, J. P. *Organometallics* 1993, 12, 2832.

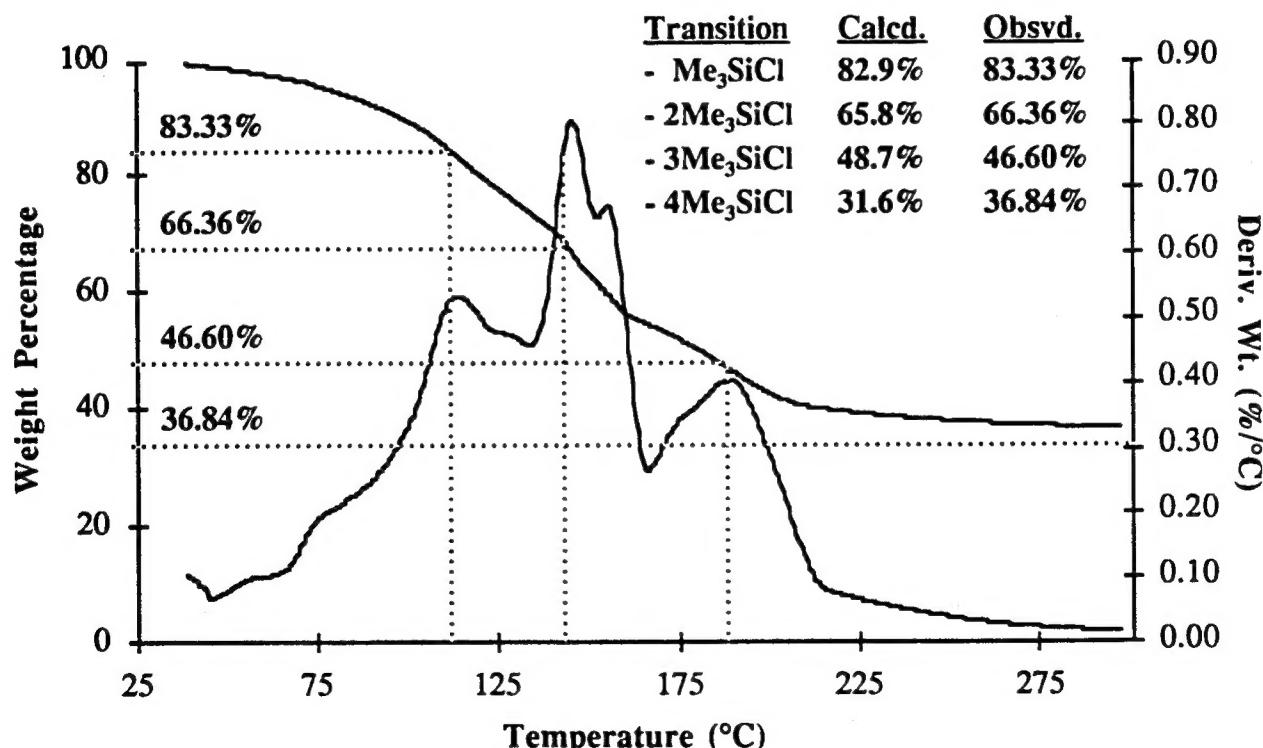
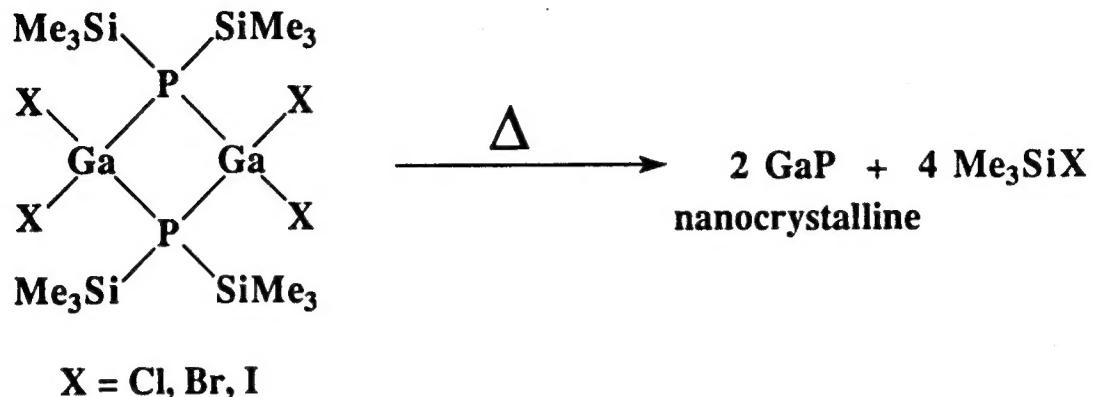
**Aubuchon, S. R.; McPhail, A. T.; Wells, R. L.; Giambra, J. A.; Bowser, J. R.**  
*Chem. Mater.* 1994, 6, 82.

## **Solid-State Synthesis of Polycrystalline III-V Semiconductors**



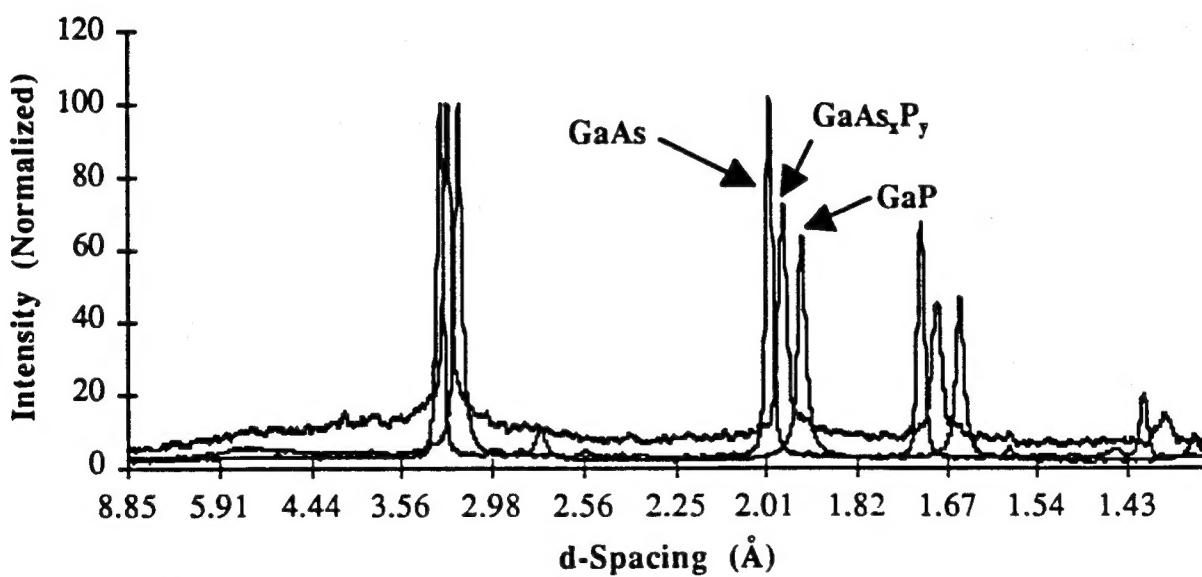
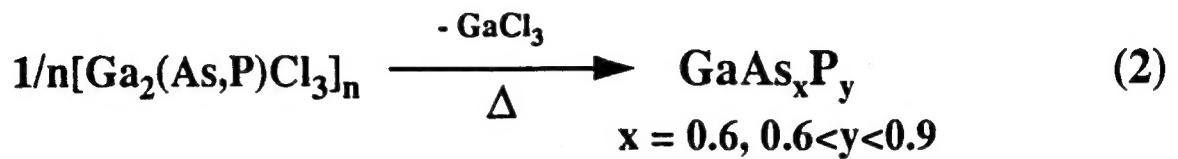
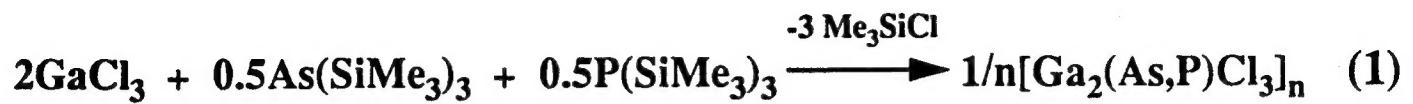
Kaner and co-workers (a) *Chem. Mater.* 1992, 4, 9 (b) *Mater. Res. Soc. Symp. Proc.* 1992, 271, 169; (c) *Science* 1992, 255, 1093; (d) *Inorg. Chem.* 1993, 32, 2745.

**Research Highlight:  
Decomposition Studies**



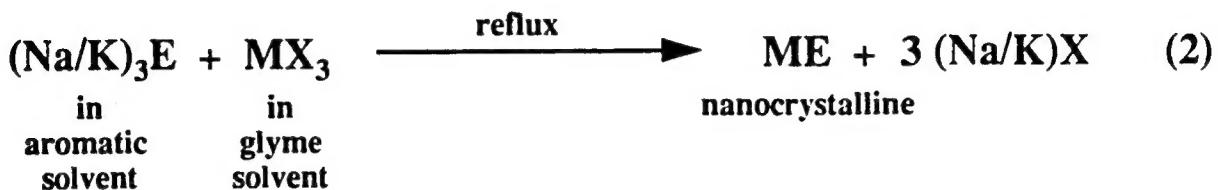
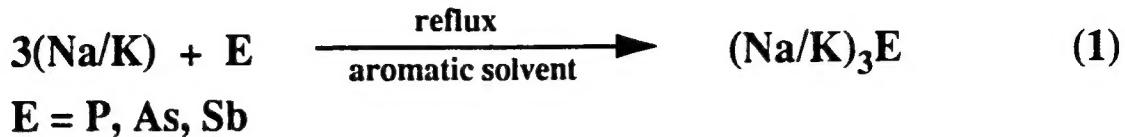
TGA of  $[\text{Cl}_2\text{GaP}(\text{SiMe}_3)_2]_2$

**Research Highlight:  
New Ternary III-V Single-Source Precursor**



**XRD Powder Patterns**

**Research Highlight:**  
**New, Low Temperature Solution Phase**  
**Synthesis of III-V Quantum Dots**



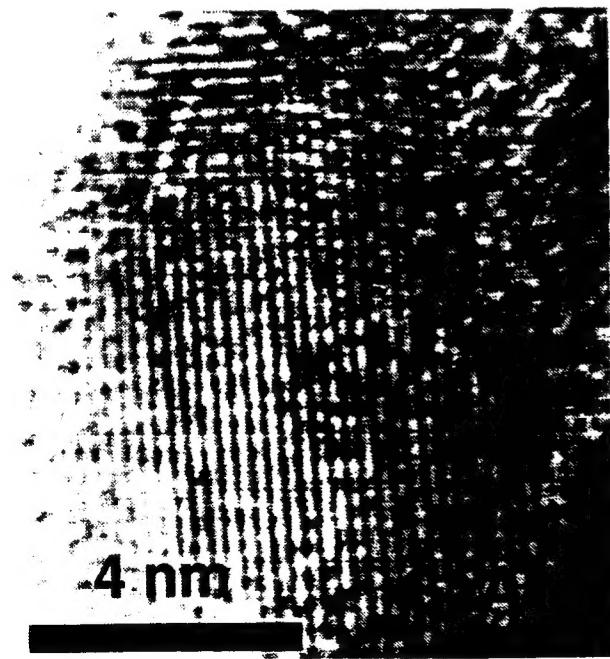
$\text{M} = \text{Ga, X} = \text{Cl, I}$

$\text{M} = \text{In, X} = \text{I, Cl, Br}$

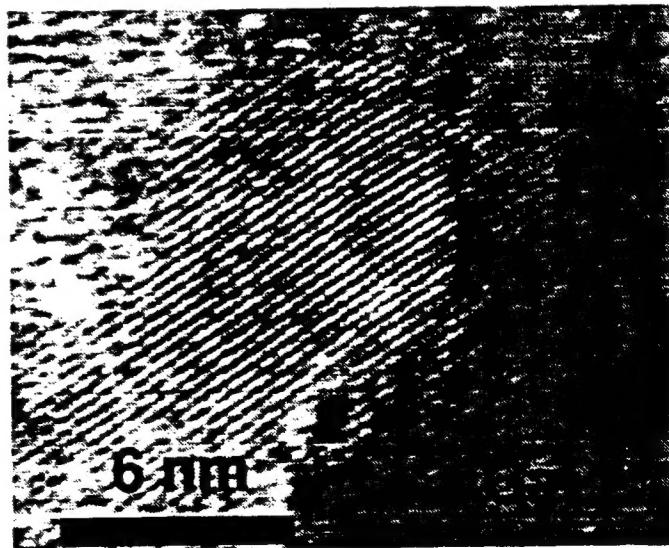
Kher, S. S.; Wells, R. L. *Mater Res. Symp. Proc.* 1994, 351, 293.

Kher, S. S.; Wells, R. L. *Chem. Mater.* 1994, *in press*.

Kher, S. S.; Wells, R. L. *U.S. Patent Application Serial No. 08/189,232*, filed Jan. 31, 1994, *pending*.



TEM



TEM

## Research Highlight: Characterization and Immobilization

- Rigorous, multi-technique characterization of GaAs Quantum Dots
  - X-Ray Diffraction (average crystallite size)
  - TEM & SEM (extent of aggregation; lattice planes)
  - Multi-Point BET (surface area and particle shape)
  - STM (nanoscopic conductivity and morphology)
  - Photoluminescence (band gap; quantum confinement)
  - Voltammetry (extent of surface oxidation)
  - XPS (surface elemental composition)
- Immobilization of GaAs, GaP, InP and InAs
  - solvent casting on electrode surfaces
  - immobilization in conducting organic films of poly(pyrrole)

### ***STM Images:***

- A.** poly(pyrrole)
- B.** InAs on Pt
- C.** InAs in poly(pyrrole)

